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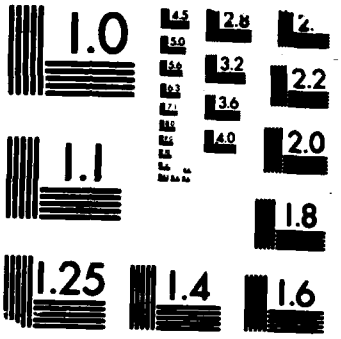

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Heat-treated benzene-derived graphite fibers have been characterized by Raman spectroscopy as a function of applied uniaxial tensile stress. Linear shifts are observed in the frequency of the Raman lines as a function of the applied stress. Thus it is shown that laser Raman spectroscopy provides a powerful nondestructive technique for monitoring the local stress variations near the surface of carbon fibers. The Raman microprobe used in this experiment provides approximately two micrometers spatial resolution within the optical skin depth. This spatial resolution is much higher than conventional techniques such as x-ray analysis which typically has a spatial resolution of several millimeters. Stress measurements in semiconductors such as Silicon, Germanium and Gallium Arsenide by Raman spectroscopy have been previously reported.

Since benzene-derived graphite fibers are typically between ten and 20 micrometers in diameter, Raman spectroscopy has been used to examine the stress variation within the optical skin depth (approximately 600 Angstroms for light scattering at 4880 Angstroms) of single carbon fibers.

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STRESS MEASUREMENTS IN GRAPHITE FIBERS BY LASER RAMAN SPECTROSCOPY[1]

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Introduction

Laser Raman spectroscopy is a powerful nondestructive technique for monitoring the local stress variations near the surface of materials. The Raman microprobe used in this experiment provides $\sim 2\mu m$ spatial resolution within the optical skin depth. This spatial resolution is to be contrasted with more conventional techniques such as x-ray analysis which typically have a spatial resolution of several millimeters. Stress measurements in semiconductors such as Si[1], Ge[2] and GaAs[2] by Raman spectroscopy have been previously reported.

Graphite fibers are currently of interest to materials applications requiring high strength to weight ratio. However, no stress measurements in graphite fibers by Raman spectroscopy have been reported, though Raman measurements of the in-plane optical lattice mode have been shown to provide a sensitive method for the characterization of the structural perfection of carbon fibers[3,4]. Since the benzene-derived graphite fibers[5] are typically between 10 and $20\mu m$ in diameter, Raman spectroscopy can be used to examine the stress variation within the optical skin depth ($\sim$ 600Å for light scattering at 4880Å).

In this work, heat-treated benzene-derived graphite fibers are characterized by Raman spectroscopy as a function of applied uniaxial tensile stress. Linear shifts are observed in the frequency of the Raman lines as a function of the applied stress.

Experimental Procedure

The carbon fibers used in the present investigation were prepared on a substrate by pyrolyzing a mixture of benzene and hydrogen at a temperature of $\sim$ 1100°C. After the growth, graphitization of the fibers is accomplished by heat treatment at a temperature of 2900°C using a carbon-resistance furnace in a high-purity argon atmosphere. The resulting fibers consist of concentric graphite layers around the fiber axis, such as the annular rings of a tree [5]. The fiber diameter used in this work was $7.6\mu m$ and the fiber length was 15 mm. Single fibers were bonded to the sample stage of the Raman microprobe at one end and to a nylon string which was connected to a pan containing weights at the other end. Uniaxial tensile stress was applied to the fibers by putting weights on the pan and thus the stress direction was coincident with the fiber axis.

The Raman scattering measurements were made at room temperature in the backscattering configuration using a Raman microprobe [6] with 488 nm Ar^+ laser excitation, a 40X objective lens (about $1\mu m$ spot size) and a diode array detector. The Raman spectra were taken for polarizations such that the electric vectors of the incident beam were either parallel or perpendicular to the stress direction of the fibers. Spectra were also taken for more than 8 points at random along the fiber axis at each stress level. The values of the peak position and half-width in the Raman spectra were determined by a Lorentzian fit to the experimental points.

Results and Discussion

The doubly degenerate Raman mode at about 1580cm^{-1} which corresponds to the Raman-allowed E_{2g2} mode in HOPG was used for the Raman characterization. The disorder-induced line at about 1360cm^{-1} could barely be detected in the Raman spectra of the fibers used, indicating a nearly complete graphitization of the fibers and a nearly full establishment of three-dimensional graphite ordering[7].

Figure 1 shows a plot of the Raman shift for the peak near 1580cm^{-1} as a function of the uniaxial tensile stress σ. The stress σ is applied along the fiber axis, while the electric vector E of the incident beam is polarized either parallel or perpendicular to the stress direction, that is, $\sigma \| E$ and $\sigma \perp E$, respectively. The Raman shift of HOPG is also presented in this figure as a reference and it can be seen that the Raman shift of the fibers in the absence of stress is within 1 cm^{-1} of that of HOPG. From our data in Fig. 1, it follows that the Raman shift decreases linearly with increasing σ in both cases ($\sigma \| E$ and $\sigma \perp E$) and the decrease in the case of $\sigma \| E$ is significantly faster than that of $\sigma \perp E$. The different behavior for the two polarizations corresponds to the splitting of the double degeneracy of the E_{2g_2} mode under uniaxial stress.

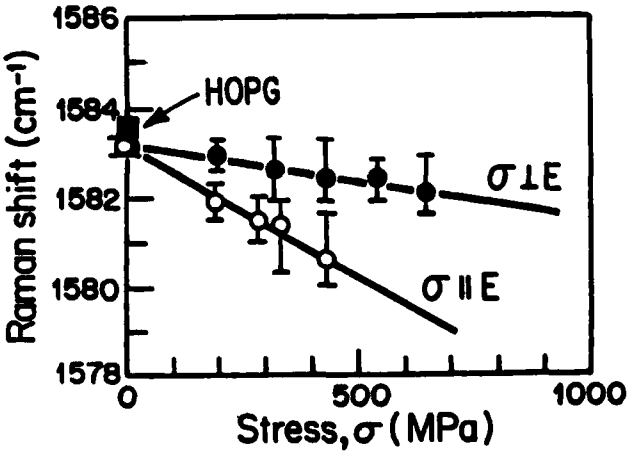

Figure 1: Plot of the Raman shift for the peak near 1580cm^{-1} vs. the applied uniaxial tensile stress σ.

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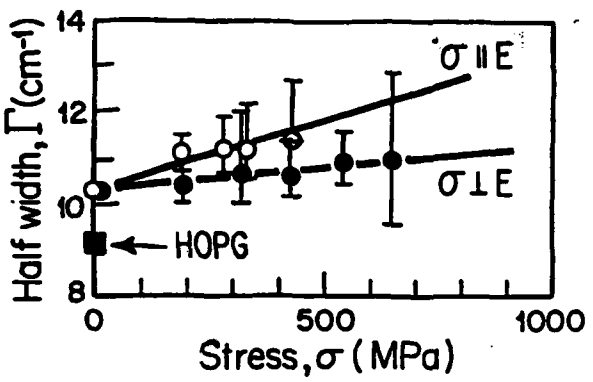

Figure 2: Plot of the half-width Γ for the peak near $1580cm^{-1}$ vs. the applied uniaxial tensile stress σ.

The variation in the half-width Γ at half maximum intensity of the $1580cm^{-1}$ lines as a function of σ for the two polarization directions is shown in Fig. 2. The half-width Γ of the fibers in the absence of stress is slightly larger than that of HOPG. From Fig. 2, it can be seen that the half-width Γ increases linearly with increasing σ for both polarizations and the increase in the case of $\sigma \| E$ is slightly faster than that of $\sigma \perp E$. These half-width variations correspond to the inhomogeneous variation of the local stress or strain distribution.

Figure 3 shows a plot of the shift $\Delta\omega = \omega_0 - \omega_\sigma$, where ω_0 and ω_σ are the Raman shifts in the absence and presence of stress, respectively, as a function of σ. The data for diamond $(\sigma \| [100], \sigma \perp E)$[8] and semiconducting materials such as Si[1], Ge[2] and GaAs[3] $(\sigma \| [111], \sigma \| E)$ are also presented in Fig. 3. From Fig. 3, it follows that $\Delta\omega$ for the fibers increases linearly with increasing σ for both polarizations and the increase of $\Delta\omega$ in the case of $\sigma \| E$ is about 3.5 times larger than that of $\sigma \perp E$. Thus the stress σ is related to $\Delta\omega$ by the following equations:

$$\sigma(MPa) = 168 \cdot \Delta\omega(cm^{-1}); \quad \sigma \| E \qquad (1)$$

$$\sigma(MPa) = 588 \cdot \Delta\omega(cm^{-1}); \quad \sigma \perp E \qquad (2)$$

These experimental measurements should be useful in engineering applications since the local stress can be estimated nondestructively by measurement of $\Delta\omega$. It can also be seen

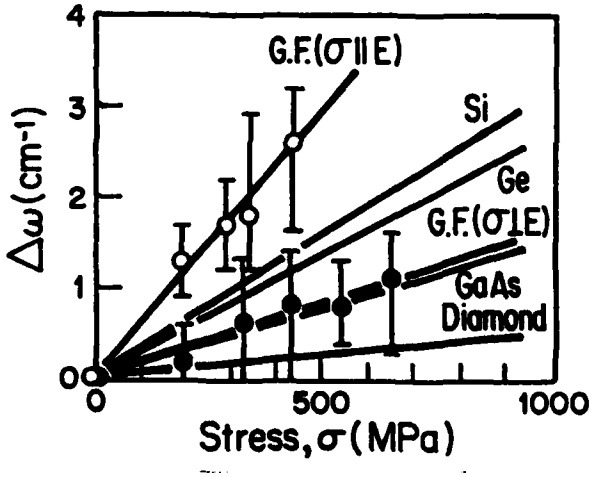

Figure 3: Plot of $\Delta\omega = \omega_0 - \omega_\sigma$ vs. the applied uniaxial tensile stress σ for graphite fibers (G.F.) and typical semiconductors.

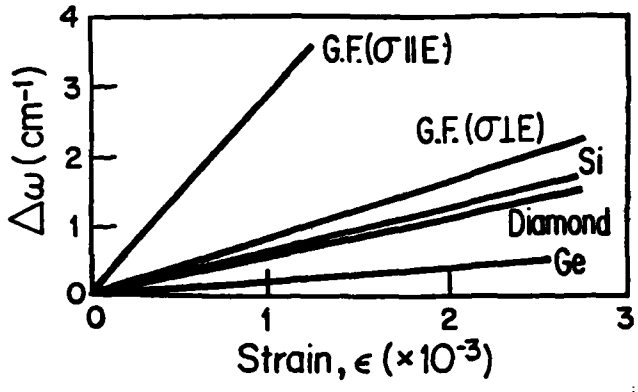

Figure 4: Plot of the experimental shift $\Delta\omega$ vs. the calculated strain ϵ, which is estimated from the elastic modulus.

that the increase $\Delta\omega$ for the benzene-derived graphite fibers is comparable to that for other materials shown in Fig. 3. We have been unable to obtain this measurement on crystalline graphite.

The relationship between $\Delta\omega$ and the strain ϵ which is calculated from the elastic modulus and the applied stress is shown in Fig. 4, where it is found that the strain dependence of $\Delta\omega$ for the graphite fibers is somewhat larger but comparable to that for typical semiconducting materials.

From this Raman scattering study of the characterization of heat-treated benzene-derived graphite fibers under stress, it is concluded that Raman spectroscopy can be used to provide complementary information on the local stress conditions of these fibers. Stress-induced changes in the Raman spectra of graphite fibers as a function of heat treatment temperature and fiber diameter will be investigated for graphite fibers synthesized from benzene vapor. A study of the effect of intercalation on air stable intercalants will be undertaken.

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